Art. XVI.—*Preliminary Survey of Eucalyptus-Oils of Victoria.*

By W. Percy Wilkinson.

[Communicated by C. R. Blackett, Esq., F.C.S., &c., 14th December, 1893].

Only of recent years have the Eucalyptus-Oils, both in their purely chemical and commercial aspects, been receiving the attention they deserve, considering that large tracts of the continent of Australia are covered with forests of the Eucalypts, including more than 134 species (Baron F. von Mueller, 2nd *Systematic Census of Australian Plants*, Part I., 1889; *Eucalyptographia*, 1879-1884), many of which yield much volatile oil. Hitherto the oils have been investigated almost exclusively in Europe, where however only limited varieties of the oils have been accessible; so it seemed to me that, as a detailed examination of certain typical oils was being carried out by European chemists, the most advantageous work to begin on in Australia would be a general preliminary examination of the oils from as many distinct Eucalypts as possible. Accordingly eighty-seven samples were gathered (practically all in Victoria), some from the Botanic Garden Museum, some from the Pharmaceutical Society's Museum, and the rest directly from the distilleries, which during the last few years have increased greatly in number. It was an essential part of the inquiry to ascertain the botanical source of as many of the oils as possible, and in a number of cases it has been with great kindness determined by Baron F. von Mueller, our distinguished Government Botanist, on specimens submitted to him. For the purposes of a general preliminary examination it was desirable to select a few definite physical properties capable of exact measurement for defining and differentiating the oils, and the density, specific rotation, refractive index and specific refractive energy were chosen as most suitable; the boiling points of the oils were not taken, as their range is small, and because the boiling points of mixtures such as these oils is not a satisfactory physical constant. The only chemical test applied

to all the oils has been Cahours' nitrite reaction for Phellandrene (*Ann. der Chem.* 41, p. 76), as modified by Bunge (*Zeit. für Chem.* 5.; *Bull. Soc. Chim.* 1870, pp. 272-273) and Wallach and Gildemeister (*Ann. der Chem.* 246, p. 282).

The densities were taken with a pyknometer holding about 25 grammes of water, and in each case at 15°C., referred to water at 15°C. The specific rotation was measured in a column of liquid 10 c.m. in length at 15°C., using the Sodium-flame; if a is the angle of rotation and d the density, then the specific rotation in the usual notation is

$$[\alpha]_D = \frac{a}{d}.$$

The refractive index was measured at 20°C. for the D line of Sodium with a spectrometer read to minutes but not to fractions of a minute, the index in each case being calculated from three independent measurements of the angle of deviation δ according to the usual formula

$$\mu = \frac{\sin. \frac{A+\delta}{2}}{\sin. \frac{A}{2}}$$ where A is the angle of the prism.

To obtain the specific refractive energy $\frac{\mu_D - 1}{d}$ at 20° $\left(\frac{\mu-1}{d}\right.$ being only slightly variable with temperature$\left.\right)$, the densities at 20° were calculated from those determined at 15° by means of the formula $d_{20^\circ} = d_{15^\circ}(1 - 5b)$ where b is the coefficient of change of density of the oil for 1°C.; b was determined for four oils by means of measurements of their densities at 15° and 100°C. as now given.

TABLE I.

$d_{\cdot 15^\circ}$	$d_{\cdot 100^\circ}$	b
·8532	·7846	·000945
·8753	·8072	·000916
·9134	·8411	·000931
·9213	·8481	·000934
	Mean. ...	·000931

The values of the physical constants are given in the following table for the 87 Eucalyptus-Oils, arranged in the order of ascending density :—

TABLE II.

EUCALYPTUS-OILS.

Progressive Number.	Botanical Source.	Density $15°/15°$	Specific Rotation $[\alpha]_D^{15°}$	Refractive Index $\mu_{\cdot D}^{20°}$	Specific Refractive Energy $\frac{\mu_D - 1}{d}$	Phellandrene Reaction.
1	E. amygdalina - -	·8532	−88·9°	1·4758	·5603	P
2	,, ,, - -	·8544	−82·5°	1·4765	·5603	P
3	,, ,, - -	·8560	−80·7°	1·4758	·5584	P
4	,, ,, - -	·8561	−73·9°	1·4769	·5596	P
5	,, ,, - -	·8568	−81·1°	1·4781	·5606	P
6	,, ,, - -	·8582	−71·1°	1·4769	·5583	P
7	,, ,, - -	·8625	−69·5°	1·4813	·5606	P
8	,, ,, - -	·8641	−63·6°	1·4789	·5570	P
9	,, ,, - -	·8695	−68·5°	1·4829	·5580	P
10	,, ,, - -	·8726	−36·2°	1·4725	·5439	P
11	,, citriodora - -	·8745	0·0°	1·4527	·5200	N
12	,, amygdalina - -	·8750	−35·9°	1·4745	·5447	P
13	,, ,, - -	·8753	−56·3°	1·4813	·5524	P
14	,, ,, - -	·8767	−68·4°	1·4785	·5483	P
15	,, ,, - -	·8777	−84·0°	1·4777	·5467	P
16	,, ,, - -	·8789	−44·6°	1·4749	·5428	P
17	,, ,, - -	·8806	−42·6°	1·4717	·5381	P
18	,, citriodora - -	·8817	−58·4°	1·4793	·5461	P
19	,, dumosa - - -	·8842	+ 0·6°	1·4701	·5341	S.pt.
20	,, amygdalina - -	·8884	−55·7°	1·4761	·5383	P
21	,, ,, - -	·8893	−16·3°	1·4713	·5323	P
22	,, ,, - -	·8894	−70·8°	1·4789	·5410	P
23	,, ,, - -	·8894	−64·9°	1·4757	·5373	P
24	,, ,, - -	·8908	−56·1°	1·4797	·5410	P
25	,, ,, - -	·8925	−35·3°	1·4829	·5435	P
26	,, ,, - -	·8940	−22·4°	1·4693	·5273	P
27	,, ,, - -	·8942	−17·8°	1·4701	·5281	P
28	,, pauciflora - -	·8943	+16·7°	1·4629	·5200	N
29	,, globulus - -	·8958	+17·3°	1·4641	·5205	N
30	,, amygdalina - -	·8967	−59·9°	1·4869	·5454	S.pt.
31	,, cneorifolia - -	·8991	−13·3°	1·4677	·5226	S.pt.
32	,, oleosa - - -	·9066	+ 5·5°	1·4624	·5124	N
33	,, cneorifolia - -	·9071	−12·1°	1·4705	·5211	N
34	,, Mallee (mixed var.) -	·9081	+ 5·5°	1·4580	·5067	N
35	,, gracilis - - -	·9090	+ 9·3°	1·4612	·5097	N
36	,, globulus - -	·9120	+ 1·1°	1·4596	·4952	N
37	,, rostrata - -	·9120	+ 8·7°	1·4604	·5072	N
38	,, globulus - -	·9125	+ 3·8°	1·4612	·5077	N
39	,, ,, - -	·9127	+ 4·9°	1·4632	·5098	N

Progressive Number.	Botanical Source.	Density $15°/15°$	Specific Rotation $[\alpha]_D$ $.15°$	Refractive Index $\mu_{\cdot D}^{20°}$	Specific Refractive Energy $\frac{\mu_D - 1}{d}$	Phellandrene Reaction.
40	E. piperita	·9133	+ 1·6°	1·4592	·5051	N
41	„ Mallee (mixed var.)	·9134	+ 2·7°	1·4608	·5068	N
42	„ globulus	·9142	+ 1·1°	1·4793	·5465	S.pt.
43	Eucalyptol	·9143	+ 4·1°	1·4608	·5063	N
44	E. Mallee	·9145	+ 3·8°	1·4608	·5062	N
45	„ amygdalina	·9148	− 3·3°	1·4612	·5064	N
46	„ globulus	·9152	− 6·2°	1·4580	·5027	N
47	„ dumosa	·9152	+ 6·8°	1·4624	·5074	N
48	„ Leucoxylon	·9154	+ 0·7°	1·4634	·5085	N
49	„ oleosa	·9155	+ 5·2°	1·4629	·5080	N
50	„ dumosa	·9159	+ 6·5°	1·4829	·5296	N
51	Eucalyptol	·9161	+ 3·8°	1·4616	·5062	N
52	E. Leucoxylon	·9164	+ 0·5°	1·4596	·5037	N
53	„ amygdalina	·9168	− 35·9°	1·4801	·5260	P
54	„ Stuartiana	·9175	− 7·1°	1·4709	·5156	N
55	„ (mixed var.)	·9175	+ 4·9°	1·4616	·5054	N
56	„ (mixed var.)	·9192	− 2.2°	1·4624	·5053	N
57	„ globulus	·9196	+ 2·2°	1·4596	·5020	N
58	„ goniocalyx	·9197	− 4·3°	1·4705	·5140	N
59	„ globulus	·9197	+ 4.4°	1·4632	·5060	N
60	„ pauciflora	·9200	+ 6·0°	1·4604	·5027	N
61	„ citriodora	·9200	0·°	1·4612	·5036	N
62	„ cneorifolia	·9200	− 2·7°	1·4640	·5066	N
63	„ globulus	·9202	+ 2·7°	1·4592	·5013	N
64	„ „	·9207	+ 2·7°	1·4612	·5032	N
65	„ (mixed var.)	·9209	+ 0·5°	1·4649	·5071	N
66	Eucalyptol	·9213	+ 3·8°	1·4604	·5020	N
67	E. cneorifolia	·9215	− 5·4°	1·4652	·5071	S.pt.
68	„ rostrata	·9216	+ 2·2°	1·4600	·5014	N
69	Eucalyptol	·9221	+ 5·9°	1·4559	·4965	N
70	E. cneorifolia	·9221	− 4·1°	1·4640	·5055	N
71	„ rostrata	·9222	+ 0·5°	1·4607	·5018	N
72	„ Lehmanni	·9236	+ 5·9°	1·4616	·5021	N
73	„ occidentalis	·9236	+ 2·7°	1·4628	·5034	N
74	„ diversicolor	·9240	+ 9·7°	...	...	N
75	„ globulus	·9265	+ 3·2°	1·4624	·5013	N
76	„ oleosa	·9267	Too dark to observe	1·4729	·5126	N
77	„ Leucoxylon	·9271	+ 2·7°	1·4608	·5000	N
78	„ fissilis	·9282	0·°	1·4592	·4970	N
79	Black Oil (Redistilled)	·9311	− 41·8°	1·4845	·5226	S.pt.
80	E. Stuartiana	·9327	− 16·6°	1·4844	·5222	S.pt.
81	Eucalyptol	·9341	+ 6·9°	1·4620	·4968	N
82	„	·9382	+ 5·6°	1·4661	·4989	N
83	Black Oil (Redistilled)	·9403	− 15·9°	1·4877	·5208	S.pt.
84	E. globulus	·9430	+ 2·1°	1·4636	·4938	N
85	„ amygdalina	·9507	− 5·8°	1·4928	·5205	S.pt.
86	„ globulus	·9512	+ 1·6°	1·4628	·4877	N
87	„ amygdalina	·9651	− 10·9°	1·4821	·5016	S.pt.

First, as regards density, it will be noticed that it ranges from ·853 to ·965, and if the last five oils, Nos. 83-87 (on account of probable alteration with age) and the two preceding Eucalyptols are omitted, the range is from ·8532 to ·9327, which is not inconsiderable. Separating out the numbers of oils whose densities lie within the ranges ·85 to ·86, ·86 to ·87, and so on, we get

TABLE III.

Density - - -	·85 *to* ·86	·86 *to* ·87	·87 *to* ·88	·88 *to* ·89	·89 *to* ·90	·90 *to* ·91	·91 *to* ·92	·92 *to* ·93	above ·93
No. of Oils - -	6	3	7	7	8	4	24	19	9

The first point to notice in this last table is, that up to a density of ·91 the numbers of oils are fairly evenly distributed through the successive intervals of ·01 in density, while at the two higher intervals from ·91 to ·92 and ·92 to ·93 the numbers increase markedly; 35 oils have their density between ·85 and ·91, while 24 have a density between ·91 and ·92, and 19 between ·92 and ·93, so that there is a tendency towards a classification of the oils by density.

Second, as regards specific rotation, it may be stated that on the whole a progressive alteration of the specific rotation accompanies the alterations of density, the lightest oils having the greatest lævo-rotation, which diminishes with increasing density to 0 at about a density of ·907, after which with a few exceptions the oils are slightly dextro-rotatory.

Third, as to refractive index, the alteration here is also progressive, the lighter oils having the higher index, which diminishes with increasing density except in the last few oils, which are altogether exceptional; but the specific refractive energy is much the better form in which to study the relations of the oil to light, and the specific refractive energies of the oils show a range of variation which is larger than that of the density, the values progressing from about ·56 to ·49 (diminishing with increasing density).

Fourth, as to the Phellandrene reaction, it will be seen from the table that all the oils which give the Phellandrene reaction

are of low density and lævo-rotatory, though some few that are lævo-rotatory do not give the Phellandrene reaction.

These results are in harmony with the general conclusions so far obtained in the study of the chemistry of the Eucalyptus-Oils, the chief result of which is to show that these oils contain two main ingredients of different densities, rotation and specific refractive energies; differences in the proportion of the ingredients producing such differences as are recorded in the tables. The researches of Wallach (*Ann. der Chem.*, 225 et seq.; *Ber der Deut. Chem. Ges.*, 24) have established that the two main ingredients are a Terpene or mixture of closely related Terpenes $C_{10}H_{16}$, and Cineol (Eucalyptol) $C_{10}H_{18}O$. The values of the above physical constants for some of these Terpenes and Cineol are approximately as follow, the values of different authorities varying too much to allow of any but approximate values being given :—

Table IV.

		B.Pt.	$d_{15°}$	$\frac{\mu_D - 1}{d}$
Cineol		176°	·9275	·495
Terpenes	Limonene	172° - 179°	·848	·562
	Pinene	155° - 160°	·862	·544
	Phellandrene	170°	·856	·560

The range of density ·848 to ·927 corresponds closely to that pointed out as holding in the natural Eucalyptus-Oils, namely ·853 to ·933, and the range of specific refractive energy is ·495 to ·562, to be compared with the range ·49 to ·56 of the natural oils. Thus it is quite clear that in the Eucalyptus-Oils as a whole we have to do with mixtures in varying proportions of bodies of the two types, Cineol $C_{10}H_{18}O$ and Terpene $C_{10}H_{16}$.

To determine which of the many isomerides possible for both of these types are really present in any one oil, the methods of investigation developed by Wallach will have to be applied; but at present it can be seen that the values of physical constants give a good measure of the relative proportions of the ingredients $C_{10}H_{18}O$ and $C_{10}H_{16}$.

As regards compounds other than $C_{10}H_{18}O$ and $C_{10}H_{16}$ in Eucalyptus-Oils, Sesqui-terpenes $C_{15}H_{24}$ appear to be present, and certain Aldehydes have been observed in quantity sufficient to give a characteristic smell to various oils, and in the case of the oil of *E. maculata* (var. *citriodora*) Citronellal (Citronellon) and Geraniol are present; but the chief work to be done in the immediate future ought to be confined to characterising and isolating the great variety of isomerides of the two main substances $C_{10}H_{18}O$ and $C_{10}H_{16}$. That to do this will be no light undertaking may be gathered from the study of Wallach's work, although he has so simplified the confusion existing as to the number of Terpenes and their derivatives. The closeness of the boiling points of Cineol, Limonene and Phellandrene shows that the method of fractional distillation can give but little help towards even a preliminary separation of a Eucalyptus-Oil into separate chemical compounds; and a brief account of two series of systematic fractionations, carried out on two typical oils, will make this clear. As it is important to realise that other methods of separation will have to be resorted to in working out the chemistry of the Eucalyptus-Oils, as has been done in certain cases by Wallach, the following tables are given to show the amount of separation achieved by a thorough fractionation. Of the two typical oils chosen the first was of the Terpene type, with low density and high negative specific rotation, and the second of the Cineol type, of high density and small positive specific rotation. To secure steadiness in the fractionations a special apparatus was put together, consisting of a copper flask of 350 c.c. capacity, with brazed joints and a neck 12 c.m. long and 19 m.m. diam.; this was inclosed in a cubical chamber of asbestos-millboard of 16 c.m. edge; into the neck of the flask was inserted by means of a thin perforated cork a ⊢ tube contracted for insertion in the flask, the large limb of the ⊢ tube was 23 m.m. diam. and the side tube 5 m.m. The ⊢ tube was enclosed in a wooden chamber with a mica-front, through which could be read the fractionating thermometer divided into $\frac{1}{5}$°C., wholly immersed in the wide limb of the ⊢ tube. The burner, which heated the cubical asbestos-chamber, was protected from draughts by a sheet-iron case. The apparatus was found to attain the desired end of

causing the thermometer readings to rise quite steadily during a fractionation.

Of the oil number 1 in Table II., 250 c.c. were twice distilled from calcium chloride to dry it, the end product being clear and almost colourless, with a dark, strongly-smelling residue left in the flask. The physical constants were slightly altered by distillation, the values being

Density ...	...	·8484$^{15°/15°}$
Specific rotation	...	$[\alpha]_D - 85·4°$
Refractive index	...	... μ_D 1·4769
Sp. ref. energy	...	... ·5637

Of the distillate 200 c.c. during one complete fractionating in the above apparatus gave the following fractions, of which the physical constants were determined as before, except the density, which was measured by a Westphal specific gravity balance; some of the fractions were so small that the measurements could not be conveniently made.

TABLE V.

$t°$ C.	Per-centage.	Density 15° / 15° C.	$[\alpha]_D$	$\frac{\mu_D - 1}{d.}$
Below 170	·7	...	...	...
170-172	3·7	·845	...	·5600
172-173	5·8	·846	− 84·6°	·5646
173-174	14·5	·846	− 84·0°	·5630
174-175	20·8	·846	− 84·6°	·5641
175-176	19·8	·846	− 88·1°	·5646
176-177	11·5	·847	− 86·3°	·5650
177-178	5·0	·849	− 83·7°	·5645
178-179	5·0	·850	− 81·3°	·5637
179-180	2·5	·854	− 73·3°	·5616
180-185	5·3			
185-195	1·8	...	...	...
Above 195	3·6	...	...	...

These numbers show that a process of separation is going on, as the density increases and the rotation varies with rising boiling point. To see how far this separation could be carried, the 11 individual fractions boiling between 155° and 195°C. were

each redistilled with the same intervals of temperature as before, when the boiling point of the first of the above fractions reached 170°; the second was added, and when the b.p. rose to 172° the third, and so on; the distillates from each fraction being collected for the intervals of temperature given in the following table, which represents the final result after several complete repetitions of the above operations.

TABLE VI.

$t°$ C.	Per-centage.	Density 15° / 15° C.	$[\alpha]_D$	$\frac{\mu_D - 1}{d}$
155-170	1·8	...	...	...
170-172	6·3	·844	− 71·8°	·5601
172-173	7·9	·845	− 83·6°	·5610
173-174	9·5	·845	− 84·9°	·5633
174-175	17·5	·847	− 92·2°	·5645
175-176	10·9	·848	− 91·5°	·5648
176-177	14·5	·849	− 87·6°	·5648
177-178	6·8	·849	− 83·2°	·5658
178-179	3·3	·850	...	·5652
179-185	5·4	·853	− 72·4°	·5642
185-195	5·0	·859	− 55·2°	·5606
Above 195	11·1	...	...	...

The process of separation noticed in the first fractionation is still going on, as again indicated by increasing densities and varying rotations. To ascertain how far this separation had gone, the Phellandrene test was applied to the fractions 155 - 170°, 179 - 185°, and 185 - 195° (Wallach and Gildemeister, *Ann. der Chem.*, 246, p. 282). The three fractions gave the Phellandrene reaction strongly, the test tubes presenting a solid mass of crystals of Phellandrene nitrite $C_{10}H_{16}.N_2O_3$.; after washing with water, then absolute methyl alcohol, and crystallising from chloroform, the crystals melted at 103°C. (m. pt. 103° - 104°C. Wallach and Gildemeister, ibid.); this is sufficient to show the practical impossibility of the satisfactory fractional separation of the Terpenes present. Attempts to prepare Bromine addition compounds from the three fractions 170 - 172°, 176 - 177°, and 185 - 195° by Wallach's method (*Ann. der Chem.*, 227, p. 280) were unsuccessful in each case; only oily compounds

separated, which refused obstinately to crystallise even when strongly cooled. The crystalline addition compounds of the Terpenes with two molecules H.Cl. (Wallach, *Ann. der Chem.*, 239, p. 3) could not be obtained from the four fractions boiling at 170 - 172°, 172 - 173°, 174 - 175°, and 179 - 185°, only liquid hydrochlorides resulting. This is in agreement with the experience of Wallach and Gildemeister in their research on *E. amygdalina* oil (*Ann. der Chem.*, 246, pp. 278-284).

The fraction 175 - 176° is of interest on account of its high specific rotation $[\alpha]_D - 91{\cdot}5°$ and low density ·843 ; after removing the Phellandrene the remaining oil is still strongly lævo-rotatory, the optical activity being probably partly due to lævo-limonene.

For studying the behaviour of the other type of oil in the fractionating apparatus, a sample of number 34 of Table II. was taken and distilled from calcium chloride with slight alteration of the physical constants as in the last case, the values being :

Density	...	...	...	$\cdot 909.^{15°/15°}$
Specific rotation	...	...	$[\alpha]_D + 5{\cdot}5°$.

A slight yellow colour in this oil should be mentioned. Several fractionations on 200 c.c. were carried out in the manner described for the other type of oil. The results of the first and final operations being given in the two following tables :—

Table VII.

t°C.	Per-centage.	Density 15° / 15° C.	$[\alpha]_D$.	$\frac{\mu_D - 1}{d}$
160-170	4·0	·898	...	·5150
170-171	11·8	·903	+ 11·6°	·5137
171-172	13·5	·904	+ 10·5°	·5131
172-173	16·8	·907	+ 8·7°	·5114
173-174	13·0	·909	+ 6·2°	·5102
174-175	12·0	·912	+ 4·4°	·5070
175-177	17·3	·915	+ 1·5°	·5055
177-179	6·0	·918	− 0·5°	·5047
179-185	3·5	·919	...	·5054
185-190	1·7	...	...	...
Above 190	0·4	...	...	...

TABLE VIII.

t° C.	Per-centage.	Density 15° / 15° C.	$[\alpha]_D$.	$\frac{\mu_D - 1}{d}$
160-170	10·0	·893	+ 18·1°	·5190
170-171	9·5	·897	+ 15·6°	·5166
171-172	7·3	·902	+ 11·7°	·5125
172-173	6·8	·906	+ 9·1°	·5100
173-174	11·8	·910	+ 6·6°	·5072
174-175	11·5	·913	+ 3·7°	·5051
175-177	26·8	·917	+ 1·3°	·5029
177-179	8·0	·920	− 0·9°	·5025
179-185	4·1	·921	− 2·7°	·5408
185-190	1·0	...	...	...
Above 190	2·2	...	...	..

The colour of the original oil appeared almost all in the first fraction 160 - 170°. The result here is as before to show clearly enough that we are dealing with a mixture of substances, the change in the specific rotation from a fairly large positive value at 160 - 170° to a small negative one at 177 - 179° being specially noticeable as accompanying an increase of density. As the oil was chosen as a typical Cineol-oil, the best method of determining how far a separation had been accomplished was to test for Cineol in each fraction according to the method of Wallach (*Ann. der Chem.*, 227, p. 280); in every case the characteristic unstable splendid prismatic crystals of Cineol di-bromide were formed, readily decomposing on exposure to the air.

Dry hydrogen chloride also produced in each of the well-cooled fractions white crystals of the unstable Cineol di-hydrochloride. From the results it will be seen, as in the first type of oil, that we are dealing with a mixture, in which fractionating effects only a limited separation.

On account of the difficulty of separating the two chief constituents of Eucalyptus-Oils by fractional distillation, it seemed to be advisable to use the measurements of the physical constants to obtain at least an approximate estimate of the proportions in which they are present. For instance, in the case of the density, if we assume that an oil is composed of p_1 parts by weight of a mean Terpene of density ·855, and p_2 parts of Cineol of density

·927, and if on mixture the shrinkage is negligible, as in the case of most mixed liquids, then the density d of the mixture is given by

$$\frac{p_1 + p_2}{d} = \frac{p_1}{d_1} + \frac{p_1}{d_2} \quad (1).$$

If $p_1 + p_2$ is 100, then $p_1 = 100 \dfrac{\frac{1}{d} - \frac{1}{d_2}}{\frac{1}{d_1} - \frac{1}{d_2}}$ (2);

so that from the density d it is possible to calculate the percentage by weight p_1 of the Terpene. Of course as a mean value ·855 is adopted for density of Terpene, while the actual densities range from ·848 to ·862; this formula should not be applied to mixtures containing only a small proportion of Cineol. If the Terpene present is known, then in the above formula its density must be taken as d_1; the mean value ·855 being used only when the nature of the Terpene is unknown.

To verify the applicability of the above formula to mixtures of Terpenes and Cineol the following mixtures were made and their densities determined for comparison with those calculated by the formula above.

Mixture I.—Equal volumes of turpentine with $d_1 = ·866$ at 15°C. and Cineol $d_2 = ·9213$ at 15°, density of mixture ·8936 at 15°, calculated value ·8936; the agreement being absolute it follows that formula (2) would give absolutely the percentage of Terpene and Cineol actually mixed.

Mixture II.—Three vols. of turpentine $d_1 = ·866$ and one vol. of oil No. 34. $d_2 = ·9081$ at 15°, density of mixture found $d = ·877$ at 15°, calculated by (1) ·879; conversely using (2) to calculate first the percentage of the two ingredients by weight, we get 26·2 Eucalyptus-Oil and 73·8 of turpentine, which corresponds to one volume of oil to 2·8 of turpentine instead of the 1 to 3 by experiment.

These two experiments show that given an oil consists of only a Terpene and Cineol the proportions of these can be obtained with a certain amount of accuracy by a single determination of the density of the oil, and if the density of the Terpene present is known, then the formula will allow its amount to be determined with fair accuracy by a single determination of the density of the oil.

This determination of the proportions of the two ingredients from the density of the mixture can be controlled by a similar calculation in connection with the specific refractive energy. It is well known, that if r_1 and r_2 are the specific refractive energies of two substances present in proportions p_1 and p_2 by weight and r the sp. ref. energy of the mixture

$$(p_1 + p_2)\, r = p_1\, r_1 + p_2\, r_2.$$

$$\text{and } p_1 + p_2 = 100, \text{ then } p_1 = 100\, \frac{r - r_2}{r_1 - r_2}$$

According to this formula the sp. ref. energies ought to vary steadily with the densities, if the oils consisted of two main ingredients, and they do vary steadily on the whole, but with marked exceptions, showing that individual oils cannot be taken as mixtures of only the two main substances. By applying the two formulæ (density and sp. ref. energy) to the measurements for an oil, it can be ascertained by the agreement of their results whether the oil is a mixture of a Terpene and Cineol or not.

As another physical constant, whose measurement might be expected to give definite indications as to the proportions of the two main ingredients in a Eucalyptus-Oil, the viscosity seemed promising, as the viscosity of Cineol at ordinary temperatures would naturally be expected to be much larger than that of a Terpene, seeing that it is much nearer its solidifying point; thus, to test the applicability of measurements of viscosity to the analysis of the Eucalyptus-Oils, the following experiments were made.

A cylindrical glass separator of 170 c.c. with a tap at the bottom had 40 c.m. of circular capillary tube connected to it by an india-rubber joint. The whole was so arranged that the capillary hung vertically from the separator, so that its upper end was 30 c.m. from the mark on the neck of the separator to which the oil was filled up in every case. The time was noted for 20 c.c. to run through the capillary; under these circumstances the viscosity is proportional to the time taken and to the density of the liquid; to obtain the specific viscosity referred to, water at 16·5°C. as 100, all that is necessary is to multiply 100 times the time taken by any oil by its density, and to divide by the time for water. The following are the results for certain oils and mixtures :—

TABLE IX.

Substance.	Time in Minutes.	Density 15° /15° C.	Specific viscosity (Water at 16·5° = 100).
Turpentine - - - -	29·0	·866	148
Oil, No. 10 - - - -	31·0	·873	159
„ „ 13 - - - -	30.0	·875	154
„ „ 34, 1 vol. - - Turpentine, 3 vols. - -	31·8	·877	164
Oil, No. 15 - - - -	30·0	·878	155
„ „ 34, 1 vol. - - Turpentine, 1 vol. - -	33·0	·883	171
Oil, No. 34, 3 vols. - - Turpentine, 1 vol. - -	34·0	·889	180
Cineol 1 vol. - - Turpentine, 1 vol. - -	38·5	·893	202
Oil, No. 41, 1 vol. - - „ „ 13, 1 vol. - -	40·0	·8936	210
„ „ 34 - - - -	40·0	·908	214
„ „ 41 - - - -	57·0	·913	306
No. 66, Cineol - - -	56·0	·921	303

It will be seen, that there is a wide range in the values of the viscosity for the different oils and mixtures, from 148 for turpentine to 303 for Cineol, moreover that a body like oil No. 13, which according to its density and specific rotation must be almost exclusively Terpene (Phellandrene), has the viscosity 154 near that of turpentine, while the oil No. 41, which according to its density contains a large amount of Cineol, also has a large viscosity, viz., 306, which indeed is too large for even pure Cineol, so that probably small amounts of still more viscous substances than Cineol are present. With only slight irregularities the viscosity rises with increasing density. From the densities the amount of Cineol in each oil or mixture can be approximately calculated as already explained, and, as increasing density means increasing content of Cineol, the viscosity rises with increasing content of Cineol.

It thus appears that conclusions drawn as to the composition of an oil from its density and specific refractive energy could be controlled in a general way by viscosity determinations.

Appendix.

Bibliography of Recent Literature on the Terpenes and their Derivatives:

Wallach and Brass, *Ann. der Chem.*,	**225.**	1884.	pp.	291-314.
Wallach, „ „	„	„	„	314-318.
„ „ „	**227.**	1885.	„	277-302.
„ „ „	**230.**	„	„	225-272.
„ „ „	**238.**	1887.	„	78-89.
„ „ „	**239.**	„	„	1-54.
„ „ „	**241.**	„	„	315-328.
„ „ „	**245.**	1888.	„	191-213.
„ „ „	„	„	„	241-278.
„ „ „	**246.**	„	„	221-239.
Wallach and Gildemeister, „	**246.**	„	„	265-284.
Wallach, „ „	**252.**	1889.	„	94-140.
„ and Conrady, „	**252.**	„	„	141-157.
„ and Otto, „ „	**253.**	„	„	249-267.
„ „ „	**263.**	1891.	„	129-156.
„ *Ber. der Deut. Chem. Gesell.*,	**24.**	1891.	pp.	1525-1579.
Wallach, *Ann. der Chem.* - -	**264.**	1891.	„	1-32.
„ „ „ - -	**268.**	1892.	„	197-228.
„ „ „ - -	**269.**	„	„	326-376.
„ „ „ - -	**270.**	„	„	171-203.
„ „ „ - -	**271.**	„	„	285-311.
„ „ „ - -	**272.**	1893.	„	99-125.
„ „ „ - -	**275.**	„	„	103-133.
„ „ „ - -	„	„	„	145-183.
„ „ „ - -	**276.**	„	„	296-327.
Brühl, *Ber. der Deut. Chem. Gesell.* - -		1888.	pp.	145-179.
„ „ „ „ - -		„	„	457-477.
„ „ „ „ - -		1891.	„	3373-3416.
„ „ „ „ - -		„	„	3701-3737.
„ „ „ „ - -		1892.	„	142-174.
„ „ „ „ - -		„	„	547-551.
„ „ „ „ - -		„	„	1788-1813.
„ „ „ „ - -		1893.	„	284-292.
Semmler, *Ann. der Chem.* - -	**241.**	1887.	„	90-150.

Semmler, *Ber. der Deut. Chem. Gesell.* -		1890.	pp.	1098-1103.
,, ,, ,, ,, -		,,	,,	2965-2968.
,, ,, ,, ,,		,,	,,	3556-3557.
,, ,, ,, ,, -		1891.	,,	201-211.
,, ,, ,, ,, -		,,	,,	682-685.
,, ,, ,, ,, -		1893.	,,	2254-2258.
Tilden, *Jour. Chem. Soc. (Trans.)* -		1875.	,,	514-518.
Tilden and Shenstone, ,, -		1877.	,,	554-561.
Tilden, ,, ,, ,, -		1878.	,,	80-88.
,, ,, ,, ,, -		1879.	,,	286-290.
,, ,, ,, ,, -		1884.	,,	410-420.
,, ,, ,, ,, -		1888.	,,	879-888.
Armstrong and Tilden, ,, -		1879.	,,	733-759.
Gladstone, ,, ,, ,, -		1864.	,,	1-21.
,, ,, ,, ,, -		1872.	,,	1-12.
,, ,, ,, ,, -		1886.	,,	609-623.
Kanonnikoff, *Jour. Prakt. Chemie* - **32.**		1885.	,,	497-523.
Pesci, *Jour. Chem. Soc. Abst.* -		1884.	,,	331.
,, *Ber. der Deut. Chem. Gesell.*		1886.	,,	874.
,, and Bettelli, ,, ,, ,,		,,	,,	875.
,, ,, ,, ,,		1889.	,,	108.
,, ,, ,, ,,		1891.	,,	204.
Bouchardat and Voiry, *Compt. Rend.* **106.**		1888.	,,	663-665.
,, ,, ,, **116.**		1893.	,,	1253-1255.
,, ,, ,, **117.**		,,	,,	53-56.
,, and Oliviero, *Bull. Soc. Chim.*		,,	,,	429-432.
Barbier, *Compt. Rend.*, **114.**		1892.	,,	126-128.
,, ,, ,, **116.**		1893.	,,	883-884.
,, ,, ,, ,,		,,	,,	993-994.
,, ,, ,, ,,		,,	,,	1062-1064.
,, ,, ,, ,,		,,	,,	1200-1202.
,, ,, ,, ,,		,,	,,	1459-1461.
,, ,, ,, **117.**		,,	,,	120-122.
,, ,, ,, ,,		,,	,,	177-178.
Husemann, *Die Pflanzenstoffe.* - - -	1884.			
Bornemann, *Die flüchtigen Oele des Pflanzenreiches* - - - -	1891.			